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In this Letter, the mechanism of double forming process phenomenon revealing in ZrO$_2$/HfO$_y$ bilayer resistive random access memory structure is investigated. This phenomenon caused by the formation of TiON interfacial layer can be well explained by using the energy band diagram. The TiON interfacial layer will be a tunneling barrier during the first forming process when a negative voltage applied on the device, while it will breakdown when applying a positive voltage. Besides, due to the double forming process, an asymmetric conductive filament with narrower size at ZrO$_2$/HfO$_y$ interface is formed in the device. The point for formation and rupture of the conductive filament can be confined at the ZrO$_2$/HfO$_y$ interface, and it will suppress the consumption of oxygen ions during endurance test. Therefore, high speed (40 ns) and large endurance (10$^7$ cycles) characteristics are achieved in this device structure.

Transition metal oxide (TMO) based resistive random access memory (RRAM) is one of the promising candidates to replace the current flash memory device as the next-generation nonvolatile memory application. The resistive switching (RS) phenomenon in metal oxide layer is attributed to the conductive filament consisting of migrated oxygen vacancies or ions under the applied electric field. Recently, the bilayer structure RRAM devices were proposed to improve endurance property, which revealed high performance RS than single layer devices. However, the resistance ratio between high resistance state (HRS) and low resistance state (LRS) will tend to fluctuation and decreasing during switching cycles test. This problem leads the endurance degradation for its applications. Some literature reported that the endurance degradation is caused by the consumption of available oxygen ions for participating in RS, which may be caused by the oxygen ions migrating toward electrodes and release them from the electrodes under an applying electric field.

In this study, a TaN/ZrO$_2$/HfO$_y$/TiN RRAM device was proposed for the high performance RS properties. All of those materials for making metal-insulator-metal structure were compatible with complementary metal oxide semiconductor (CMOS) processes. In addition, we found that those devices cannot execute success resistance switching after applying electric field. Consequently, a double forming process was found in this bilayer structure. The conductive filament mechanism can be used to well explain the double forming process phenomenon. It was clearly indicated that the endurance degradation can be improved by controlling the point in the interface between HfO$_2$ and ZrO$_2$ layers for formation and rupture of conductive filament. By the way, large endurance cycles (10$^7$ cycles) with about 100 times of HRS/LRS ratio under a fast speed (40 ns) were achieved in this TaN/ZrO$_2$/HfO$_y$/TiN device structure.

A 5 nm HfO$_2$ thin film as 1st RS layer was deposited on the TaN bottom electrode by sputtering at room temperature in 5 mTorr atmosphere with Ar/O$_2$ mixture gas ratio of 10:3. Subsequently, an oxygen annealing process at a furnace of 400°C with O$_2$ gas flow of 30 SCCM for 30 min was executed to improve the quality and reduce the amount of defects (oxygen vacancies) in HfO$_2$ layer. Then, a 3 nm ZrO$_2$ thin film as 2nd RS layer was deposited by sputtering at room temperature in 10 mTorr atmosphere with Ar/O$_2$ mixture gas ratio of 2:1. Finally, a 100 nm TaN top electrode with a diameter of 150 μm was deposited by sputtering at room temperature to form the TaN/ZrO$_2$/HfO$_y$/TiN architecture. The direct current (DC) electrical characteristics measurements were performed by using an Agilent B1500A semiconductor parameter analyzer, and the alternating current (AC) pulse was generated by Agilent B1530A waveform generator/fast measurement unit (WGFMU). The voltage was applied on the TaN top electrode with the TiN bottom electrode grounded.

Figure 1(a) shows the typical cross-section transmission electron microscopy (TEM) image of the TaN/ZrO$_2$/HfO$_y$/TiN bilayer RRAM device. Due to the obviously crystalline orientation formed in the TiN electrode, a thin interfacial layer TiON (~2 nm) is observed. The DC sweep electrical I-V curve of the present device is shown in Fig. 1(b). Unlike regular bipolar RRAM devices, the TaN/ZrO$_2$/HfO$_y$/TiN device reveals the double forming process phenomenon for switching its resistance from initial state (IS) to LRS. The double forming process can be well described in six steps: (1) First forming process, (2) Medium state (denoted as MS), (3) Second forming process, (4) LRS, (5) Reset process, and (6) HRS, as shown in Fig. 1(b).

Step 1 is to construct a larger size conductive filament in ZrO$_2$ layer and a thinner one in HfO$_2$ layer. The typical X-ray photoelectron spectra (XPS) analyses can confirm this

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phenomenon. The oxygen compositions of ZrO$_2$ and HfO$_2$ layers are depicted in Figs. 1(c) and 1(d), respectively. The two major peaks in these figures can be fitted for ZrO$_2$ and HfO$_2$ layers, respectively. The binding energies of the main peaks at around 531.4 and 530.9 eV are attributed to the O$^{2-}$ ions in the stoichiometric Zr-O and Hf-O bonds, respectively, while the higher energies of 532.1 eV in these figures correspond to the oxygen vacancies in ZrO$_2$ and HfO$_2$ layers, respectively. The inset tables in Figs. 1(c) and 1(d) indicate the area proportion of each peak. Due to the post oxygen annealing process treated for the HfO$_2$ layer, the percentage of oxygen vacancies existed in the HfO$_2$ layer is only 10%, whereas that in the ZrO$_2$ layer is 25%. Therefore, compared to ZrO$_2$ layer, less amount of the oxygen vacancies is stored in HfO$_2$ layer, as shown in Fig. 2(a). Besides, in our previous study, the physical size of the conductive filament in an oxygen vacancies deficient layer is narrower than that in the oxygen vacancies rich layer. Therefore, two different sizes of conductive filaments are formed and linked together to connect top electrode and TiON layer (Fig. 2(b)). However, no conductive filament is formed within the TiON layer in the step (1). It can be explained by the energy band diagram shown in Figs. 2(f)–2(h). Fig. 2(f) depicts the conduction band offset diagram. As a lot of defects (oxygen vacancies) exist in the ZrO$_2$ layer, the electrons can easily hop through it from top electrode to HfO$_2$ layer when a negative voltage is applied. Therefore, when the applied negative voltage increases to the first forming voltage (~4 V), the defects (oxygen vacancies) generate and form conductive filament in HfO$_2$ layer. According to the band diagram in Fig. 2(g), the electron passing through HfO$_2$ layer can easily slip along the tilted conduction band in TiON layer to TiN bottom electrode. Therefore, a larger current reaches to compliance current as measured in Fig. 1(b). However, the energy band will tend to be more flat when the applied voltage sweeps back to 0 V, thus the electrons located at the defects of HfO$_2$ layer will face a barrier between HfO$_2$ and TiON layers. This barrier causes a larger resistance when decreasing the applying voltage.
The property in step (2) is also shown in the HfO₂ single filament is illustrated in inset of the Fig. 3(b). Therefore, the shape of the conductive filament formed. Those results demonstrate that the device cannot switch to HRS because of a large sized conductive filament. Those oxygen vacancies will tend to migrate to form the conductive filament. The shape of the conductive filament is illustrated in inset of the Fig. 3(b). Therefore, the device cannot switch to HRS because of a large sized conductive filament formed. Those results demonstrate that the TaN/ZrO₂/HfO₂/TiN device cannot operate suitably under a single positive forming process.

After completing the first forming process, we also try a negative voltage to switch the device from MS to a much higher resistance state; unfortunately, a permanent hard breakdown occurs in it. On the other hand, a successful resistance switching for memory property is executed when a positive voltage applies on the device in MS as shown in Fig. 1(b). The successful bipolar RS characteristic with 100 cycles is shown in Fig. 3(c). Compared to the smaller set voltage (~1 V) in Fig. 3(c), a larger threshold voltage about 2.8 V is measured. Therefore, we call this process as the second forming process with a second forming voltage of 2.8 V in step (3) of Fig. 1(b). After the second forming process, the device can switch from MS to LRS, as shown in step (4). Finally, the regular reset process is effectively executed by applying a negative voltage after the double forming process steps in the present device, as shown in steps (5) and (6). Due to a positive voltage applies on the top electrode, the oxygen vacancies with positive charge in HfO₂ layer will be repelled toward bottom electrode. By the way, as described before in Figs. 2(h) and 3(b), a positive voltage applied on the device will cause a breakdown in the TiON layer. Therefore, the conductive filament will re-construct itself to a large size at near TiN and a small size at near the ZrO₂/HfO₂ interface. Besides, the size of conductive filament in ZrO₂ layer is still large because of the existing large amount of oxygen vacancies in it during step (1). Hence, an asymmetric shape of conductive filament with a weakest point located at the ZrO₂/HfO₂ interface is designed and formed in the present device, as shown in Fig. 2(c). Thus, the device switches from MS to LRS due to the formation of complete conductive filament. Finally, the repeatable resistance switching properties can be achieved in this device.

The electric field can be enhanced in the conductive filament due to its larger conductivity than other regions of the device. During the reset process, the interstitially oxygen...
ions existed in ZrO$_2$ layer will migrate to HfO$_2$ layer when a negative voltage is applied on top electrode. In addition, the current flowing through the narrowest size of asymmetric conductive filament (the ZrO$_2$/HfO$_2$ interface) will cause a serious local Joule heating in it. Consequently, the migrated oxygen ions associated with local thermal effect will easily recombine (oxidation) with oxygen vacancies at the ZrO$_2$/HfO$_2$ interface or top of the conductive filament in HfO$_2$ layer. Thus, dissolution of the asymmetric conductive filament causes it switching from LRS to HRS, as shown in Fig. 2(d). On the other hand, when a positive voltage is applied on the device in Fig. 2(e), the oxygen ions existed in HfO$_2$ layer will also tend to migrate to ZrO$_2$ layer. However, compared to HfO$_2$ layer, the conductive filament in ZrO$_2$ layer is too large to rupture it. Therefore, the device cannot switch to HRS by applying a positive voltage on it. When a positive voltage is applied on it during the set process, a soft breakdown and reduction reaction (oxygen vacancies are generated) occur in the region above top of the conduction filament in HfO$_2$ layer. The escaped oxygen ions due to generated oxygen vacancies migrate back to ZrO$_2$ layer to oxidize part of the oxygen vacancies to re-form the conductive filament. The device switches back to LRS, as shown in Fig. 2(e). Therefore, the formation and rupture point of conductive filament for RS property can be limited at a very narrow region at the ZrO$_2$/HfO$_2$ interface.

Due to the oxygen vacancies generation and recombination can be confined at the ZrO$_2$/HfO$_2$ interface except near the electrode during RS cycles test, the problem of escaping oxygen ions from electrodes$^{18}$ can be suppressed in the device. Therefore, it can be expected that the highly stable endurance characteristic can be achieved in the present device structure. Fig. 3(d) shows the high speed AC endurance property by using a pulse height of 3 V for set process and $-3.3$ V for reset process under a pulse width of 40 ns. Large endurance of more than $10^7$ switching cycles is achieved. About 100 times resistance ratio with less fluctuation between HRS and LRS is revealed in the ZrO$_2$/HfO$_2$ bilayer device. In addition, the read disturbance property under a constant voltage stress of 0.3 V at 85 °C is shown in the inset of Fig. 3(d). No degradation property in both HRS and LRS is maintained for more than 10$^4$ s.

In summary, the TaN/ZrO$_2$/HfO$_2$/TiN bilayer RRAM structure is fabricated in this study. The structure reveals the double forming process phenomenon before resistive switching cycles. The energy band diagram and conductive filament model can well explain this interesting phenomenon. Due to the formation of TiON thin layer between HfO$_2$ and TiN interface, it causes a dielectric breakdown only by using positive voltage applied on the device. An asymmetric conductive filament is formed after the double forming process, which can confine the point for formation and rupture of conductive filament at the ZrO$_2$/HfO$_2$ interface during resistive switching. It can suppress the resistance state degradation caused by escaping the oxygen ions from the electrodes. Therefore, the large endurance ($10^7$ cycles) with high operation speed (40 ns) is observed in this device structure, which is a good candidate for next generation nonvolatile memory application.

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